

CONJUGATE ADDITION REACTIONS OF
5-MESITOYLACENAPHTHYLENE

BY

FRANKLIN EDWIN MANGE

B.S., Massachusetts Institute of Technology, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

CONJUGATE ADDITION REACTIONS OF
5-MESITOYLACENAPHTHYLENE

BY

FRANKLIN EDWIN MANGE

B.S., Massachusetts Institute of Technology, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Reynold C. Fuson for suggesting this study and for his invaluable advice and guidance throughout the course of this work.

The author is grateful to the University of Illinois for a Teaching Assistantship from February, 1949 to June, 1949, for the Henry Strong Fellowship for the academic year 1949-1950 and for a University Fellowship for the academic year 1950-1951.



CONJUGATE ADDITION REACTIONS OF 5-MESITOYLACENAPHTHYLENE

INTRODUCTION

The more active Grignard reagents add in a 1,6 manner across the aromatic system of benzoyldurene to yield *p*-alkyl-benzoyldurenes (1,2). Studies on 1-mesitylnaphthalene indicate that it is possible to achieve 1,6 addition in this series also but in this case the dihydronaphthalene derivative is obtained (3).

These facts have led to a consideration of addition to compounds similar to those above but containing a *p*-vinyl group. Such a system would have the structural features which could permit 1,8 addition across an aromatic system if the electronic effects caused by the carbonyl group were great enough to be relayed through and beyond the aromatic system. A compound having these characteristics is 5-mesitylacenaphthylene.

Although only Grignard reagents have been caused to add across aromatic systems in diaryl ketones, it may be possible for other carbonyl reagents to add in a conjugate manner to such a system. The object of the present research was to explore these possibilities with respect to 5-mesitylacenaphthylene. If such an addition would take place, it would be the first recorded example of its type.

DISCUSSION OF RESULTS

5-Mesitylacenaphthylene was prepared by first condensing acenaphthene with mesityl chloride in a Friedel-Crafts reaction to yield 5-mesitylacenaphthene. This latter compound was then dehydrogenated to 5-mesitylacenaphthylene by bromination of the *peri*-bridge to yield presumably 1-bromo-5-mesitylacenaphthene followed by dehydrobromination with pyridine.

Addition of hydrogen bromide to 5-mesitylacenaphthylene

gave a monobromo derivative of 5-mesitoylacenaphthene which was shown to be identical to the one obtained by the bromination of 5-mesitoylacenaphthene. It is believed to be the 1-isomer for it evolves hydrogen bromide on heating and because the electronic effects of the carbonyl group would be expected to orient the attacking reagent to yield the 1-bromo isomer.

A Friedel-Crafts reaction of 5-mesitoylacenaphthylene with benzene gave 1-phenyl-5-mesitoylacenaphthene. This latter compound was also prepared by condensing 1-bromo-5-mesitoylacenaphthylene with benzene in the presence of aluminum chloride. Hydrogen cyanide failed to add under the conditions employed.

When 5-mesitoylacenaphthylene was allowed to react with Grignard reagents derived from benzyl chloride, *sec*-butyl bromide, bromobenzene and bromomesitylene only high-melting amorphous solids could be isolated along with oils which were obtained in some instances. When allylmagnesium bromide was employed, a yellow crystalline product was obtained which appeared to be the 1,2 addition adduct along with a high-melting amorphous product. To determine if these high-melting products were anionic polymerization products of 5-mesitoylacenaphthylene containing end groups derived from the Grignard reagents, *p*-chlorobenzylmagnesium bromide and chloride were allowed to react with 5-mesitoylacenaphthylene and the products were analyzed for chlorine. The results, however, were inconclusive.

Treatment of 5-mesitoylacenaphthylene with magnesian iodide yielded a high-melting amorphous product similar to those described above. The Reformatsky reaction on 5-mesitoylacenaphthylene failed when zinc and ethyl bromoacetate were used.

Successful addition in a 1,8 manner was achieved when 5-mesitoylacenaphthylene was treated with the Michael reagents, malonic ester and ethyl cyanoacetate. In both cases the addition adducts were hydrolyzed to the dibasic acid and then decarboxylated to yield the identical product, 1-(5-

mesitoylacenaphthenyl)-acetic acid. Piperidine added in a similar manner to yield presumably 1-piperidino-5-mesitoyl-acenaphthene which was isolated as the hydrochloride. Acetoacetic ester, fluorene and sodium ethoxide failed to react under the experimental conditions employed, while nitromethane gave an intractable gum.

BIBLIOGRAPHY

1. Fuson and McKusick, J. Am. Chem. Soc., **65**, 60 (1943).
2. Fuson and Tull, J. Am. Chem. Soc., **71**, 2543 (1949).
3. Tullio, Thesis, Doctor of Philosophy, University of Illinois, 1951.

VITA

The author was born in St. Louis, Missouri, on February 12, 1928. He received his elementary and high school education in that city and was graduated from Soldan High School in June, 1945. He attended the Massachusetts Institute of Technology and graduated from there with the degree of Bachelor of Science in September, 1948. At this time he entered the Graduate College at the University of Illinois. He held a Teaching Assistantship from February, 1949 to June, 1949, the Henry Strong Fellowship from September, 1949 to June, 1950 and a University Fellowship from September, 1950 to June, 1951.



Digitized by the Internet Archive
in 2026

